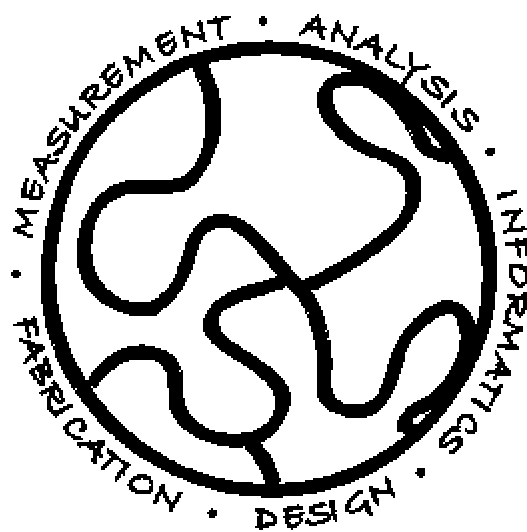


S.I.E.B.I.M.M.

Strained Induced Elastomer Buckling Instability for Mechanical Measurements

Specifications and Operation Guidelines

For the measurement of the flexural modulus of thin films and coatings



NIST Combinatorial
Methods Center

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1. Purpose and structure of this document

This document is provided by the National Institute of Standards and Technology (hereafter referred to as NIST) as a guide to constructing and operating an instrument that measures the flexural or bending modulus of thin films or coatings. First, the basic principles of this measurement technique will be described, as well as its strengths and limitations. Next, the components of the instrument and schemes for its construction are supplied. Discussion will be based largely upon the specific components and design of a measurement scheme that was developed at the NIST Combinatorial Methods Center (see disclaimer, page 1). Finally, guidelines for producing the quantitative measurements and some basic applications are outlined, including notes on computer control and automation.

2. The Mechanics of SIEBIMM

SIEBIMM (Strained-Induced Elastomer Buckling Instability for Mechanical Measurements) is based upon a few simple mechanical concepts that require little material-specific modeling. The coating to be measured is first applied to a relatively thick and soft elastomer sheet (Figure 1).



Figure 1. Schematic of SIEBIMM. The coating (red) is placed on the elastomer (yellow). Surface buckling of the bilayer takes place under compression.

Compression of the elastomer substrate (and hence the adhered coating) beyond a critical threshold produces a highly periodic buckling of the coating; the resulting wavelength is that which minimizes the compressive energy. From observations of this buckled system, the modulus of the coating (E_p) can be calculated using the following equation^{1,2,3,4}:

$$E_p = 12E_m [(3 - \nu_m)(1 + \nu_m)]^{-1} [qh]^{-3} \quad (1)$$

Equation 1 contains four measurable parameters: (1) the modulus of the elastomer (E_m), (2) the thickness of the coating (h), (3) the buckling wavenumber (q), and (4) the PDMS's Poisson ratio ν_m . The buckling wavelength d ($2\pi/q$) can be measured by one of many techniques, such as optical microscopy, light scattering, or atomic force microscopy, each of which can be automated. Measurement of the elastomer modulus (E_m) is accomplished easily with a conventional tensile testing (e.g. Instron) instrument. The thickness of the coating (h) can be obtained from the most convenient method. In the following treatment, interferometry was used since the (polymer) coatings of interest were transparent, but ellipsometry or profilometry would be equally suitable. The Poisson ratio of the PDMS (ν_m) can be approximated as $1/2$, that of an ideal elastomer.

SIEBIMM is an intrinsically local measurement. Accordingly, coating specimens that spatially vary in their properties (e.g. annealing history or ultraviolet curing history) can be

accommodated, and gradient combinatorial techniques can be leveraged. This technique has been demonstrated for films that are as thin as 20 nanometers and as thick as several microns. While the possibility was not tested, in principle this technique should be applicable to even thinner films, such as plasma deposited layers that can be a only few nm thick.

The biggest challenge in fabricating specimens for SIEBIMM is the optimization of the adhesion between the elastomer substrate and the coating to prevent delamination during buckling. In this study, polydimethylsiloxane (PDMS, here Dow Corning Sylgard 184) is employed as the substrate material. Typically, PDMS is supplied as a two-component system that can be mixed/cured in various ratios to give a transparent elastomer with tailored mechanical properties. Very thin specimen films (less than 100 nm) are sufficiently flexible such that the intrinsic tackiness of PDMS is sufficient to assure adhesion. For thicker films, or films of high modulus, greater adhesion forces are needed. This can be achieved by increasing the mixing ratio of the PDMS or by chemically bonding the coating to the PDMS. Both of these strategies will be described further below.

3. SIEBIMM Methodology

The elastomer sheets utilized for SIEBIMM can easily be cast in petri dishes or with a custom-made curing basin. To begin substrate fabrication, Dow Corning Sylgard 184 (PDMS) is vigorously mixed at the appropriate base to catalyst ratio, typically 10:1 or higher (see below). Mixing will disperse a large quantity of air bubbles, which results in a non-transparent though translucent blend. Bubbles will slowly dissipate if the mixture is allowed to degas overnight in a shallow (~1 mm deep) basin with a large surface area, though researchers pressed for time can quickly expunge the bubbles by placing the mixture under vacuum. A sufficient quantity of PDMS should be created such that the cast sheet will be at least one millimeter thick. This thickness target provides sufficient strength such that 25 mm by 75 mm slabs (typical substrate dimensions) can be conveniently handled. However, for samples that will undergo a strain greater than 20%, a stronger substrate is typically needed; in such cases a minimum sample thickness of 3 mm is recommended. For a curing basin with the dimensions (16 cm x 16 cm) shown in Figure 2, a total mass of approximately 50 grams produces a one-millimeter thick PDMS sheet. As SIEBIMM measurements are independent of the PDMS thickness, it is not vital that the thickness of the PDMS sheet be reproduced with great accuracy. It is good practice to place a piece of plate glass at the bottom of the mixing basins so that the PDMS is cured against an optically smooth surface. However, take note that if the basin glass is aggressively cleaned via UV/ozone to a hydrophilic state, PDMS will chemically bind to surface, thereby preventing the cured PDMS from being removed and effectively destroying both the sheet and the basin. After carefully pouring the PDMS into the basin, a cover should be placed over the curing PDMS to prevent airborne dust from collecting in the surface. After degassing, the PDMS is baked in a forced-air oven at 75°C for 1 hour (no vacuum is necessary) to fully cure.

Removal of the cured PDMS sheet is achieved by gently cutting the edges with a razor blade, slowly pulling out the sheet, and transferring to a clean piece of glass. The perimeter of the PDMS sheet is left in the basin, as there is typically a meniscus that forms at the edge with undesirable surface curvature. Individual PDMS substrates (e.g. 25 mm by 75 mm) are then cut from the cast sheet with a standard razor blade or with a "cookie-cutter" type of stamp. As

partially cured PDMS will continue to conform to its substrate we recommend against storing PDMS on aluminum foil or any surface which is not optically smooth. Again, care should be taken to keep PDMS covered at all times as airborne dust quickly collects on its tacky surface.

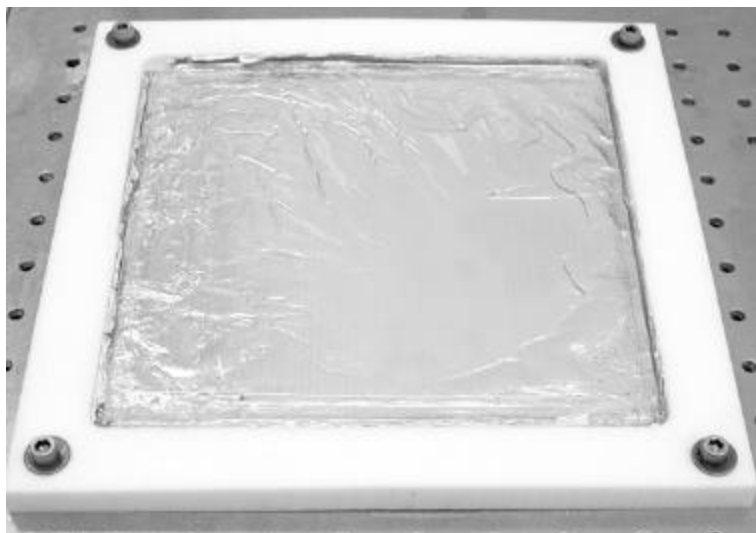


Figure 2. Casting basin for PDMS. Teflon (white) base with milled ($16 \times 16 \times 0.5$ cm³ deep) casting area bolted to optical table lined with aluminum foil. Inner basin consists of a pane of glass with a PDMS rim. A level is used to assure surface planarity during curing.

Figure 3 shows two pieces of PDMS of different thickness which were made by casting and curing. The resulting stress/strain properties strongly depend upon the mixing ratio of base and catalyst components (see Table 1 below). Moduli were measured with an Instron-style Texture Analyzer (model # TA-XT2i) by obtaining a stress/strain curve - values reported are extrapolated to the limit of zero strain. For the most accurate SIEBIMM measurement, it is important that the slope of the stress-strain curve (instantaneous modulus) be taken at the same strain used to induce buckling. This consideration plays a large role mainly for strains greater than 10%. We find that for identical mixing ratios and curing history the variability of the modulus of PDMS is less than 10%. There is a strong increase in PDMS modulus with curing time. For example an increase by a factor of 40 can increase the modulus by 40%. While we have not quantified the surface tackiness, simple tests with a gloved finger reveal that the tackiness decreases substantially with annealing time.



Figure 3. Two PDMS samples: a thick slab (10 mm) and a thin sheet (1 mm). Note the samples' transparency, which greatly assists light scattering by enabling the laser to pass directly through the PDMS without a significant amount of scattering or distortion.

The mechanical instability that SIEBIMM exploits relies upon a large mismatch of the moduli of the coating and the PDMS. We find that for glassy polymer films, or materials with moduli 200 Mpa and above, a lower mixing ratio (e.g. 10:1 base to catalyst mixture) produces substrates that are of sufficiently low modulus for effective implementation of SIEBIMM. For films or coatings with moduli below this, a higher mixing ratio (20:1 or more) is more suitable. An additional consideration is that the tackiness of the PDMS increases as the mixing ratio increases. High tackiness aids in the transfer of the film/coating from the original substrate to the PDMS as well as suppressing delamination of the buckled film. One point of concern with higher mixing ratios of PDMS is that the approximation for Poisson's ratio of $\frac{1}{2}$ may no longer be valid, but this is a minor source of error.

Table 1. Modulus of PDMS vs mixing ratio for 1 hour cure at 75°C. There was typically an overnight precure at ambient temperature. Shorter times or lower temperatures result in PDMS with a lower modulus and tackier surface.

PDMS Mixing Ratio (Mass:Mass)	Zero Strain Extrapolated Modulus (MPa)
10:1	1.5
20:1	0.5
25:1	0.25

4. Demonstration with Polymer Thin Film Thickness Library

Library Preparation: In this document SIEBIMM and its high-throughput capabilities will be demonstrated by using it to characterize the modulus of a thickness gradient specimen library (See Fig. 4). This library consists of a polystyrene thin film with a thickness gradient via flow-coating, a NCMC-developed technique described elsewhere.^{5,6} The film was cast from a toluene solution onto a single crystal silicon wafer substrate, though an optically smooth glass may also work as a substrate. Before flow-coating, the wafer surface was made hydrophilic by exposing it

to UV/ozone (Jelight model 342) for 20 minutes. This treatment will help with the transfer of the film onto the PDMS slab.

Library Characterization: After casting the gradient library, the film thickness was measured as a function of position with a Filmetrics F-20 interferometer. As also seen by the color variation in Fig. 4, the thickness library ranges from 140 nm to 240 nm (left to right). Note: by changing the concentration of the flow-coated solution thickness ranges that are higher or lower than shown here can be created. During the characterization of the thickness library and in later steps, measurement registry was achieved by using the top right hand corner of the film library as a fiduciary mark.

Transfer of Library to PDMS Substrate: This is completed in two steps. First, freshly cured PDMS substrate was then applied to the wafer as in Figure 4. Here, air trapped between the PDMS and the film can be seen on the far left and far right of the sample. Bubbles such as these can be avoided by first applying the PDMS from one end and then gradually and slowly rolling the rest of the slab onto the film specimen.

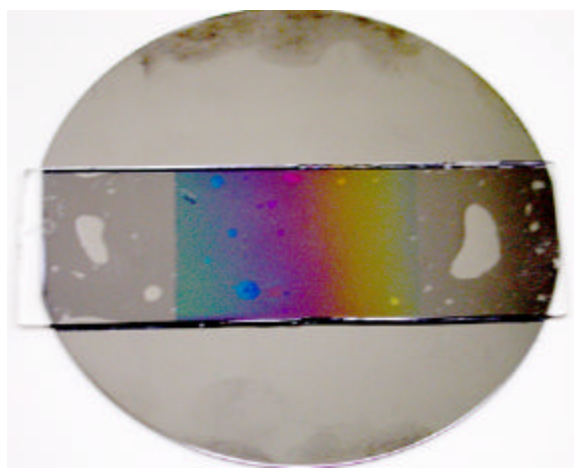


Figure 4. Thickness gradient on a three-inch silicon wafer. A 50 mm by 75 mm PDMS substrate has placed on top of the library. There are air bubbles trapped between the PDMS and the film; two large examples can be seen on the left and right.

Next, the polymer film is transferred from the wafer to the PDMS substrate. To facilitate this process, the sample (with overlying PDMS slab) was immersed in a water basin. Since the wafer has been made hydrophilic, water has a stronger affinity for the silicon wafer than the PS film, and thus aids in the transfer of the film to the PDMS. Gently tugging on edges of the PDMS sheet gently helps complete the transfer procedure. Here, the key is to use a slow, edge-wise tugging so that the PDMS that only bends the sheet a few degrees - this will minimize cracking of the polymer film. A wafer tweezer is a good tool to use in the transfer procedure. When the PDMS and film are completely released from the wafer, the PDMS substrate (with attached film) is removed from the water and placed (film side up!) onto filter paper for drying. An absorbent paper or air gun can be used to remove residual droplets of water. Depending upon the specimen

being measured, water adsorption may slightly alter its modulus, requiring a longer drying step before SIEBIMM measurements.

Straining the PDMS-mounted Library: After the film library is successfully transferred to the PDMS sheet it is mounted on a strain stage (Figure 5) with each side fastened between by the two silver clamps. Care is taken to ensure that the sample is fastened such that a uniform strain can be applied to the PDMS sheet. A Newport 850G actuator (Fig. 5, left) drives the strain stage. Detailed schematics for the strain stage assembly will be furnished upon request from the NIST Combinatorial Methods Center (combi@nist.gov).

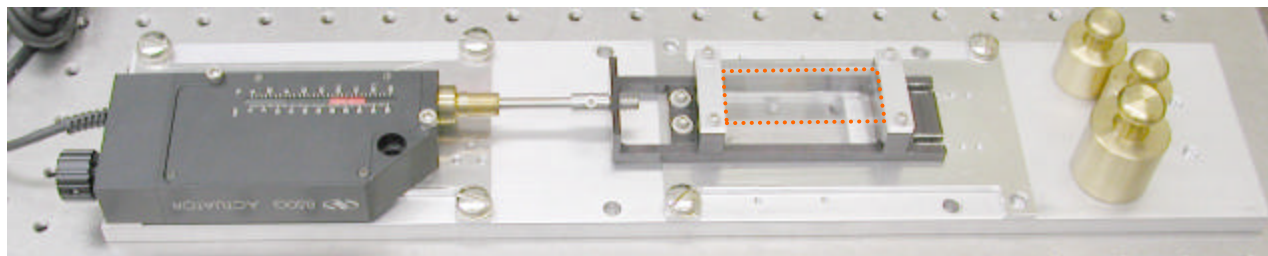


Figure 5. Strain stage. The transparent PDMS sheet (outlined with orange dashed line) is clamped between supports. The 850G actuator (black, left side) controls the magnitude of applied strain. Spacing of tapped holes at top of figure is one inch.

Elongating the sample a few percent with the 850G actuator induces buckling of the sample. Because PDMS is a material with a Poisson ratio of $\frac{1}{2}$, this results in a compression along an orthogonal direction, inducing the buckling. Optical microscopy, atomic force microscopy, or light scattering can be used to examine buckled samples mounted on this strain stage. In this demonstration, a small angle light scattering (SALS) instrument (Figure 6-8) was used to measure the buckling wavelength. The strain stage is placed onto a computer-controlled translation stage driven by custom built software tools - these Labview routines can be found on the NCMC website, www.nist.gov/combi.

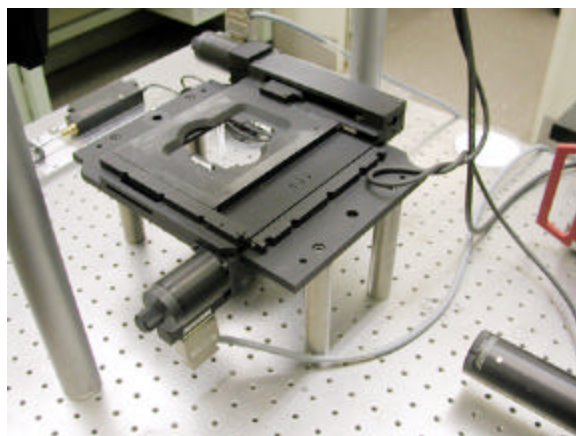


Figure 6. Translation stage without strain stage. HeNe laser tube can be seen on bottom right hand corner. Laser beam is reflected vertically through the rectangular hole in the center of the strain stage (Fig. 5).

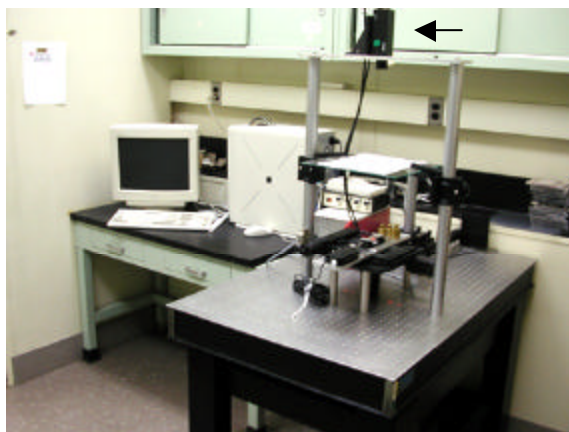


Figure 7. View of entire SALS set up. CCD camera can be seen above and computer to the left (arrow).



Figure 8. A SIEBIMM sample is strained with the 850G actuator and a HeNe laser is directed through the transparent sample in the center of the stage. Diffraction peaks are projected on the diffusion screen at top of image (circled). A CCD camera (not shown) is mounted above and collects images of the diffraction pattern. The sample has been elongated parallel to the long direction of the strain stage, resulting in a compression along the shorter dimension. Since the buckling lines run parallel to the long direction of the stage, this results in a line of diffraction peaks that run in the perpendicular direction.

As mentioned above, a Labview program has been constructed to automate the SALS measurements. In an automated experiment, the user specifies a regular grid of points over which data will be acquired and an image of the SALS diffraction pattern is acquired at each of these positions. The stage translates the sample to the correct position and then directs the CCD camera to take a picture. Complementary image analysis routines (available from the NIST Combinatorial Methods Center) extract the dominant wavenumber, q , at each position.

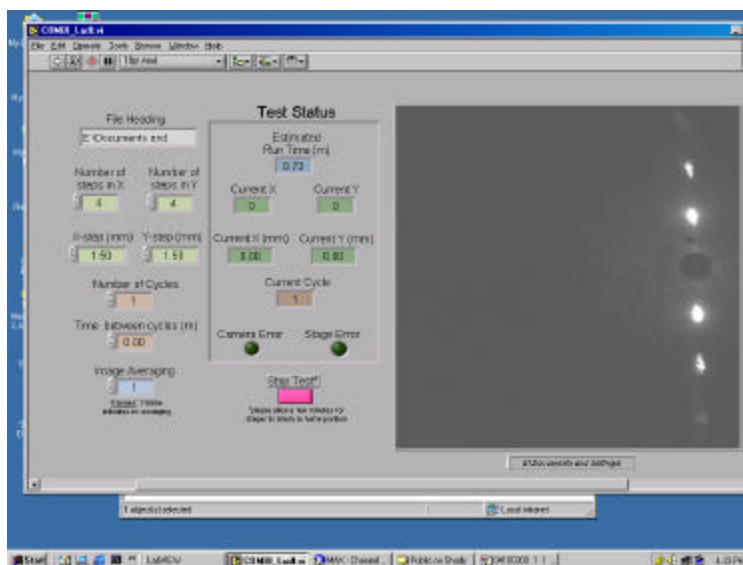


Figure 9. Screenshot of Labview program captured during data acquisition process. A portion of the diffraction pattern can be seen in the dark window in the figure. Four bright diffraction peaks are lined up in the vertical direction (positive and negative orders). A beam stop has blocked the main beam.

Figure 10a shows an enlargement of the thickness gradient on the silicon wafer. Panels b-d show optical images along the thickness gradient after the specimen was transferred to the PDMS sheet and strain was applied. Note that the buckling wavelength, as can be seen by the horizontal lines in panels b-d, increase with film thickness in good agreement with equation 1. SALS was used to measure the buckling wavelength d for each thickness and the associated modulus was calculated.

The data in Figure 11 were obtained via SALS from the sample shown in Figure 10. Here, the blue symbols show the buckling wavelength d plotted vs the local sample thickness, demonstrating the linear relationship. The buckling wavelength and film thickness yield the local film modulus E_p (red symbols), which is largely constant over this thickness range, and has an average value of 3.168 ± 0.109 GPa. Nanoindentation measurements⁷ on similar thin films, as well as conventional methods on bulk samples, agree extremely well with this data. For example, a flexural modulus bend test⁸ on bulk polystyrene samples with similar preparation histories revealed a modulus of 3.22 ± 0.05 GPa, in good agreement with SIEBIMM.

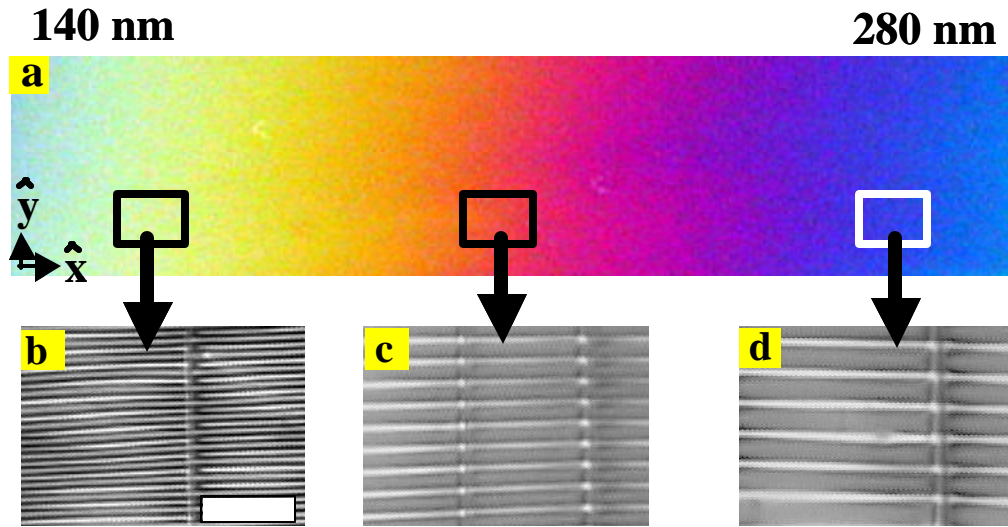


Figure 10 a) Optical image of the thickness gradient on silicon wafer. The color is determined by the local color, which increases linearly along the horizontal direction from left to right. B-d) Optical images of the film after transfer to PDMS and application of elongational strain in the horizontal direction. This leads to well-defined sinusoidal wrinkles in the horizontal direction. The wavenumber q of these periodic lines is measured by SALS.

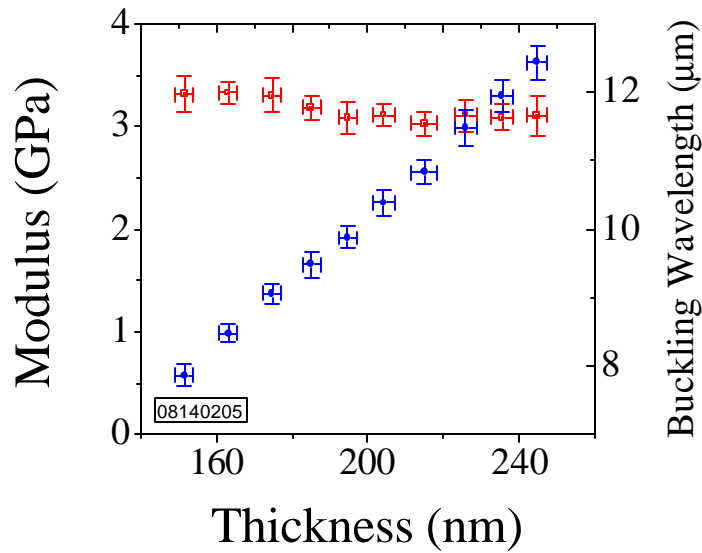


Figure 11. Buckling wavelength (blue, right axis) and calculated modulus E_p (red, left axis) for thickness gradient shown in Figure 10. Buckling wavelength increases linearly with thickness while modulus is constant within our measurement uncertainty.

5. Further Application Notes

SIEBIMM can be partnered with well-established combinatorial technologies, such as flow coating, to make a powerful high-throughput measurement strategy. Flow coating allows the fabrication of specimens with thickness gradients where the range typically spans a factor of two of thickness, e.g. from 100 to 200 nm thick, over a 4cm to 5 cm length. The SIEBIMM measurement spot size (about 1mm) is sufficiently small that the thickness change over this footprint is negligible. Accordingly, hundreds of independent modulus measurements per flow-coated sample to be collected in short period of time - about 2-3 seconds per measurement.

In this document, a thickness gradient was used to illustrate this technique's high-throughput capabilities, but one can imagine many other useful gradient approaches. For example, the modulus and hardness of UV-cured coatings depends upon the magnitude of the applied UV dose. By combining a UV gradient (see NIST UV-Ozone Gradient Instrumentation, NIST Combinatorial Methods Center, www.nist.gov/combi) with SIEBIMM, one could measure the modulus over a wide range of UV dose in a single sample. Similarly, a temperature gradient can be used to produce annealing or processing conditions that vary over a film. Moreover, two gradients can be combined in an orthogonal manner to produce a specimen library that explores every combination of two parameters, and SIEBIMM can be used to quickly measure the mechanical properties of each case.

While it is customary to transfer the film library to a relaxed PDMS strip, occasionally it is advantageous to transfer the specimen to a "pre-stressed" PDMS substrate. In this alternative sample preparation route, a controllable compression is achieved by gradually decreasing the distance between supports on the strain stage. Through this method, buckling can be achieved without cracking the film, which can be important for brittle specimens.

Experience demonstrates that many polymeric and metallic materials can be transferred from hydrophilic substrates onto PDMS using the water submersion technique. However, it should be noted that annealing (or other processing steps) can sufficiently increase adhesion between the substrate and coating such that transfer is prevented. For cases in which annealed specimens are desired, a water-soluble salt plate (Wilmat catalog #100A10) can be employed as a sacrificial substrate. In this scheme, the specimen is deposited on the salt plate and annealed/processed as necessary. Since thickness measurements are easier on a reflective substrate, a parallel specimen (produced with identical parameters) can be produced on a silicon wafer. A PDMS slab is applied to the film on the salt plate and the system is immersed in water. As a result, the salt is dissolved and the film is left on the PDMS. If this technique does not work, the film can be chemically bonded to the PDMS. Strategies for achieving this bonding can be found in the work of Whitesides and coworkers.⁹

Finally, we note that an alternative PDMS casting basin can be made with 10 by 10 by 100 mm glass strips glued to plate glass, arranged with a 10 mm spacing (Figure 12). These cuboids can be more useful in some cases for triggering the mechanical instability without a strain stage. Such cuboids can be very useful for demonstration purposes.



Figure 12. Alternative casting basin to make a thick PDMS cuboid shown above and in Figure 3.

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